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Synthesis of a New 92 K Superconductor (Ca, Sr)₃Cu₂C_{0.75}O_y with a 4a-type Superstructure

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A new 92 K superconductor has been synthesized using high pressure. A single phase with a nominal composition (Ca_{0.3}Sr_{0.7})₃Cu₂C_{0.75}O_y was obtained by heating at 1,473 K under 6 GPa for 30 minutes. A tetragonal unit cell with $a=3.851$ Å and $c=10.941$ Å, and orthorhombic supercell of $a\times 4a\times 2c$ were found by X-ray power diffraction and electron diffraction. The supercell is probably a result of carbon vacancies along the b -axis. The sample had a large Meissner volume fraction at 5 K and the temperature dependence of resistivity is metallic from room temperature to 92 K. Irreversibility field was measured as a function of temperature up to 5 T.

KEY WORDS: Ca-Sr-Cu-C-O system/ Oxide Carbonate Superconductor/ High-Pressure Synthesis/ Irreversibility Line

1. INTRODUCTION

Several cupric oxide high T_c -superconductors containing carbon in a $A_2(\text{Cu, C})\text{O}_3$ type 'block' layer (A : alkaline earth elements) have recently been reported.¹⁻⁴⁾ The prototype composition is Sr_2CuCO_5 , and its solid solution $(\text{Sr, Ba})_2\text{Cu}_{1+x}\text{C}_{1-x}\text{O}_y$ becomes superconducting at 34 K.²⁾ More complex oxide carbonates containing double CuO_2 sheets, such as $(\text{Y}_{0.86}\text{Sr}_{0.14})\text{Sr}_2\text{Cu}_2(\text{Cu}_{0.6}\text{C}_{0.4})\text{O}_y$,⁵⁾ were also found, and a compositional modification to $(\text{Y}_{0.5}\text{Sr}_{0.5})_{0.95}\text{Sr}_{2.05}\text{Cu}_2(\text{Cu}_{0.4}\text{C}_{0.6})\text{O}_y$ rendered it superconducting at 63 K.⁴⁾ Subsequent studies using a high-pressure synthesis technique have realized a series of compounds with a general formula $A_{n+1}\text{Cu}_n\text{CO}_y$ up to $n=4$. Particularly in the case of $A=(\text{Ca, Ba})$, a maximum T_c of 117 K was reported for $\text{Ba}_2\text{Ca}_3\text{Cu}_4(\text{Cu}_{0.5}\text{C}_{0.5})\text{O}_y$ with $n=4$.⁶⁾ On the other hand, compounds with $A=(\text{Ca, Sr})$ prepared at 5 GPa were made superconducting at 50 K ($n=1$), 105 K ($n=2$) and 115 K ($n=3$) by partially replacing quadrivalent carbon ions by trivalent boron ions.⁷⁾ We have been exploring the $A\text{-Cu-O}$ system by using a high-pressure technique for a few years⁸⁻¹¹⁾ and noticed that an intended doping of carbon leads to a 92 K superconductor, an $n=2$ member without any rare-earth elements nor boron as above.

In this paper, we report the high-pressure synthesis of $A_3\text{Cu}_2\text{CO}_y$ for $A=\text{Sr}$ and $(\text{Ca}_{0.3}\text{Sr}_{0.7})$ and structural investigations by means of powder X-ray diffraction (XRD), electron diffraction (ED) and high-resolution electron microscopy (HREM).

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2. EXPERIMENTAL

Starting materials were mixtures of CuO , Sr_2CuO_3 or $(\text{Ca}_{0.3}\text{Sr}_{0.7})_2\text{CuO}_3$, CaCO_3 and SrCO_3 . The precursors Sr_2CuO_3 and $(\text{Ca}_{0.3}\text{Sr}_{0.7})_2\text{CuO}_3$ were prepared from CuO , CaCO_3 and SrCO_3 at 1,273 K in air. Two series of nominal compositions were examined; $\text{A}_3\text{Cu}_{2+x}\text{C}_{1-x}\text{O}_y$ and $\text{A}_3\text{Cu}_2\text{C}_{1-x}\text{O}_y$ ($\text{A}=\text{Sr}, (\text{Ca}_{0.3}\text{Sr}_{0.7})$; $0 \leq x \leq 0.25$). The starting powder was sealed in a gold capsule with or without 3 wt. % of KClO_4 , which released oxygen on heating, and was pressed up to 6 GPa using a cubic-anvil-type apparatus. Then, the sample was heat-treated at 1,473 K for 30 minutes, followed by quenching to room temperature. The pressure was released gradually after the heat treatment. The weight of the final product was about 50 mg. It was confirmed by an EDX (Energy-Dispersive X-ray) analyzer that KCl which had been produced after the decomposition of KClO_4 segregated in the final product and that the oxide carbonate particles were not contaminated by potassium nor by chlorine.

XRD measurements using monochromated $\text{Cu-K}\alpha$ radiation were used to characterize the samples. Microstructure was investigated by ED and HREM carried out with a JEOL-2000EX microscope equipped with a top entry goniometer stage operated at 200 kV. Temperature dependence of DC magnetic susceptibility was measured by a SQUID magnetometer (Quantum Design: MPMS₂ system) for powdered samples in an external magnetic field of 10 Oe. DC electrical resistivity was measured by a four-probe method with a measurement current of 10 mA.

3. RESULTS AND DISCUSSION

3.1 $\text{Sr}_3\text{Cu}_2\text{CO}_y$

A nearly single phase sample of ' $\text{Sr}_3\text{Cu}_2\text{CO}_y$ ' has been obtained from a starting composition $\text{Sr}_3\text{Cu}_{2+x}\text{C}_{1-x}\text{O}_y$ ($x=0.25$) without KClO_4 . The powder XRD pattern is shown in Fig. 1, where most of the peaks are indexed with a tetragonal cell of $a=3.91 \text{ \AA}$ and $c=10.88 \text{ \AA}$. $\text{Sr}_4\text{Cu}_6\text{O}_{10}$ ⁹⁾ coexisted as an impurity, as can be seen in Fig. 1, if one started from a relatively copper-rich composition of $x=0.25$, while Sr_2CuCO_5 appeared in place of $\text{Sr}_4\text{Cu}_6\text{O}_{10}$ for a starting composition of $x=0$. Judging from the lattice constants and the intensity profile of the

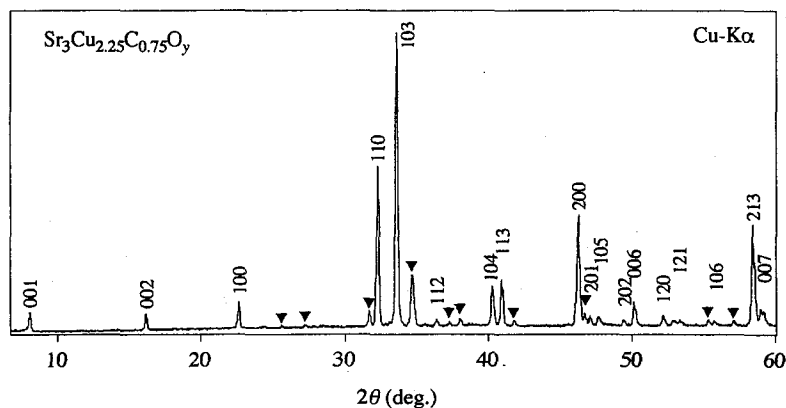


Fig. 1. XRD pattern of a sample prepared from a starting composition of $\text{Sr}_3\text{Cu}_{2.25}\text{C}_{0.75}\text{O}_y$. The extra peaks marked by triangles come from $\text{Sr}_4\text{Cu}_6\text{O}_{10}$.⁹⁾

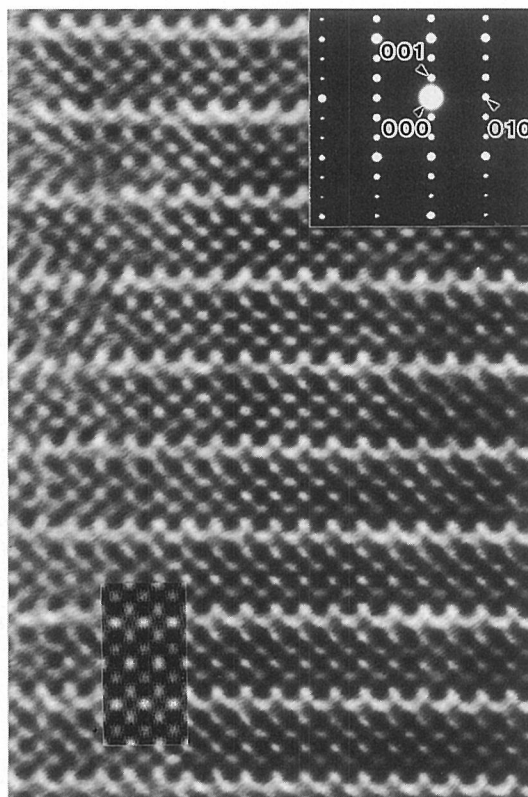


Fig. 2. HREM image and the corresponding ED pattern of the same sample as in Fig. 1. A computer-simulated image is inserted.

XRD pattern the present phase is considered to be isomorphous with $(Y_{0.86}Sr_{0.14})Sr_2Cu_2(Cu_{0.6}C_{0.4})O_y$. The high-resolution electron microscope image shown in Fig. 2 clearly exhibits that $CuO_2/Sr/CuO_2$ slabs and $Sr_2(Cu, C)O_3$ slabs alternate along the c -axis: the carbon sites correspond to the faint dark dots within the bright layers. The image was simulated by using a computer software MacTempas on the basis of the structural parameters for $(Y_{0.86}Sr_{0.14})Sr_2Cu_2(Cu_{0.6}C_{0.4})O_y$,⁵⁾ which is inserted in the real image of Fig. 2. A fairly good agreement is obtained.

The use of $KClO_4$ on preparation always decomposed the present phase, but this was not the case for the Ca-substituted phase, as will be described in the next section. All the samples prepared without $KClO_4$ showed no trace of superconductivity.

3.2 $(Ca_{0.3}Sr_{0.7})_3Cu_2CO_y$

In contrast to the Sr pure phase, a single phase sample was obtained only from a carbon deficient starting composition of $(Ca_{0.3}Sr_{0.7})_3Cu_2C_{1-x}O_y$ with $x \sim 0.25$. Moreover, it showed superconductivity at 92 K when prepared with $KClO_4$.

Figure 3 shows a series of XRD patterns for samples of $(Ca_{0.3}Sr_{0.7})_3Cu_2C_{1-x}O_y$ ($x=0.00, 0.10, 0.20, 0.25$) from the top to the bottom. In the case of the ideal composition ($x=0.00$), the sample is a mixture of two phases ' A_2CuCO_y ' (filled circles) and ' $A_3Cu_2CO_y$ ' (open circles) as

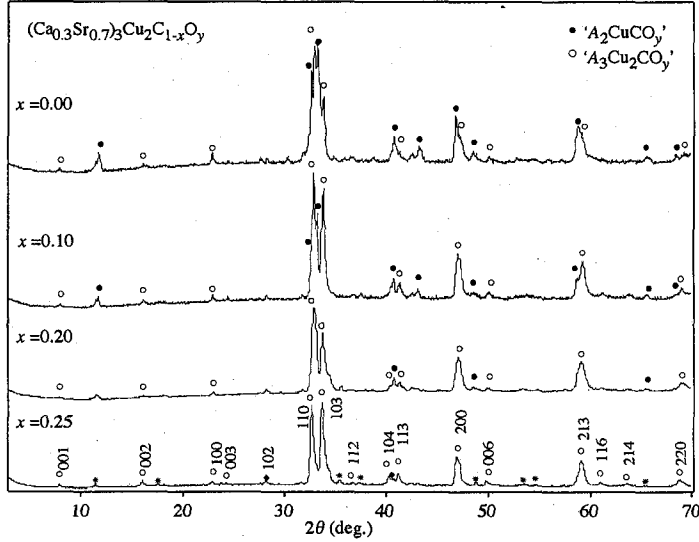


Fig. 3. A series of XRD patterns for samples prepared from starting compositions of $(\text{Ca}_{0.3}\text{Sr}_{0.7})_3\text{Cu}_2\text{C}_{1-x}\text{O}_y$ with $x=0.00, 0.10, 0.20, 0.25$. The peaks marked by open and filled circles are attributed to the ' $\text{A}_3\text{Cu}_2\text{CO}_y$ ' phase and the ' A_2CuCO_y ' phase, respectively. The small peaks marked with asterisks are due to the superlattice formation of $a \times 4a \times 2c$, and those marked with filled rhombuses are due to KCl.

seen in the top of the figure. As x increases, the ' A_2CuCO_y ' phase relatively decreases and disappears at $x \sim 0.25$. This monotonic change in the relative fraction would be natural if one assumed that a carbon deficient phase $\text{A}_3\text{Cu}_2\text{C}_{1-\delta}\text{O}_y$ is to be formed, because the carbon fraction is much larger in ' A_2CuCO_y ' than in ' $\text{A}_3\text{Cu}_2\text{CO}_y$ '.

The XRD pattern of $(\text{Ca}_{0.3}\text{Sr}_{0.7})_3\text{Cu}_2\text{C}_{0.75}\text{O}_y$ (at the bottom of Fig. 3) is indexed with a tetragonal cell of $a=3.851 \text{ \AA}$, $c=10.941 \text{ \AA}$. The extra weak peaks come from KCl (\blacklozenge) and the formation of a superlattice of $a \times 4a \times 2c$ (*) as found from electron diffraction experiments.

Temperature dependence of magnetic susceptibility of $(\text{Ca}_{0.3}\text{Sr}_{0.7})_3\text{Cu}_2\text{C}_{0.75}\text{O}_y$ shows a distinctive drop at 92 K due to a superconducting transition as seen in Fig. 4. The Meissner volume fraction estimated at 5 K is about 20% of the perfect diamagnetism which is large enough to conclude bulk superconductivity.

Temperature dependence of resistivity for the same sample is shown in Fig. 5. Normal state resistivity is $\sim 2 \text{ m}\Omega\text{cm}$ at room temperature and decreases linearly with decreasing temperature. Then it drops at $\sim 92 \text{ K}$ reaching zero within an experimental error of $10^{-3} \text{ m}\Omega\text{cm}$ at $\sim 80 \text{ K}$.

The oxidizing atmosphere during the preparation was crucial to the occurrence of superconductivity: the present phase did not show superconductivity if it was prepared without KClO_4 . A distinctive difference in lattice constants was detected between the superconducting and non-superconducting samples. The former has a shorter a -axis and longer c -axis, suggesting holes being doped.

Electron diffraction experiments have revealed that the superconducting phase has a superlattice of $a \times 4a \times 2c$. A typical ED pattern taken along the $[100]$ zone is reproduced in Fig. 6. A rectangular mesh with center spots, indicating a systematic absence due to body centering,

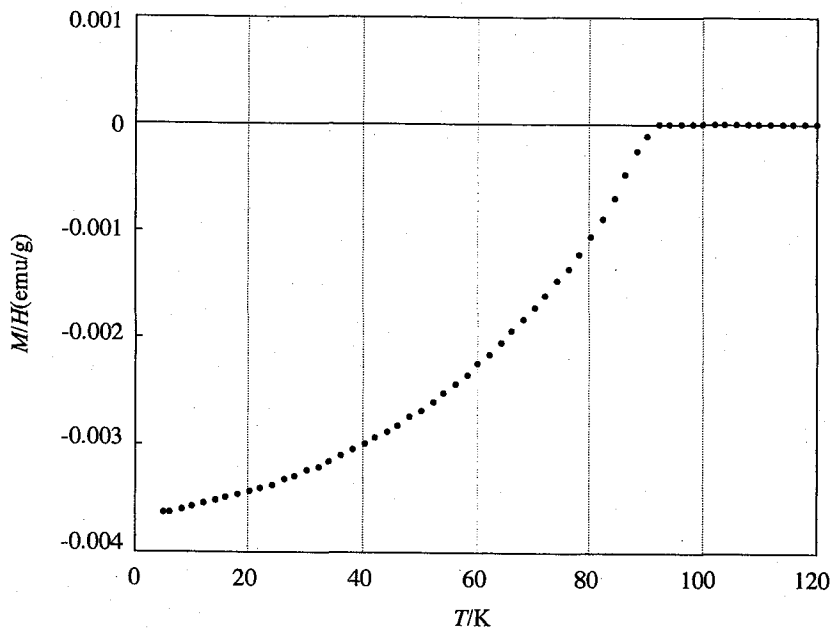


Fig. 4. Temperature dependence of DC magnetic susceptibility for $(\text{Ca}_{0.3}\text{Sr}_{0.7})_3\text{Cu}_2\text{C}_{0.75}\text{O}_y$ measured in an applied field of 10 Oe on cooling.

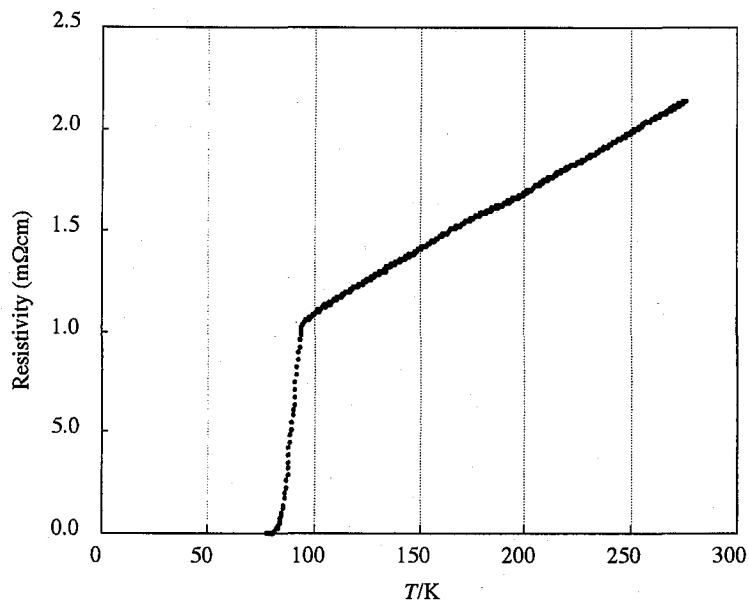


Fig. 5. Temperature dependence of electrical resistivity of $(\text{Ca}_{0.3}\text{Sr}_{0.7})_3\text{Cu}_2\text{C}_{0.75}\text{O}_y$.

is seen, having half the area of the large mesh corresponding to the fundamental cell. There were no superlattice spots along the $[010]$ zone. Thus, the true superlattice unit cell turns out to be $a \times 4a \times 2c$. The superlattice reflections observed in the XRD pattern shown in Fig. 3

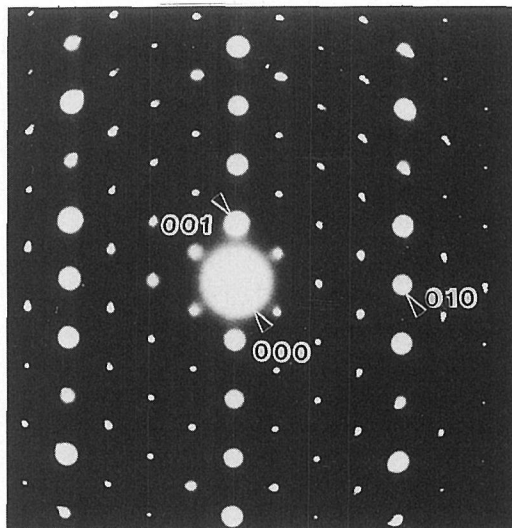


Fig. 6. Electron diffraction pattern taken along the $[100]$ zone revealing the 4 times periodicity along the b -axis.

are consistent with this interpretation.

The present superstructure is apparently different from those previously reported which are $2a$ - and $3a$ -type superstructures arising from the ordering between copper and carbon atoms within a layer. The fact that the deficiency of a quarter of carbon is necessary to obtain a single phase superconducting sample suggests that the present $4a$ -type superlattice is due to the

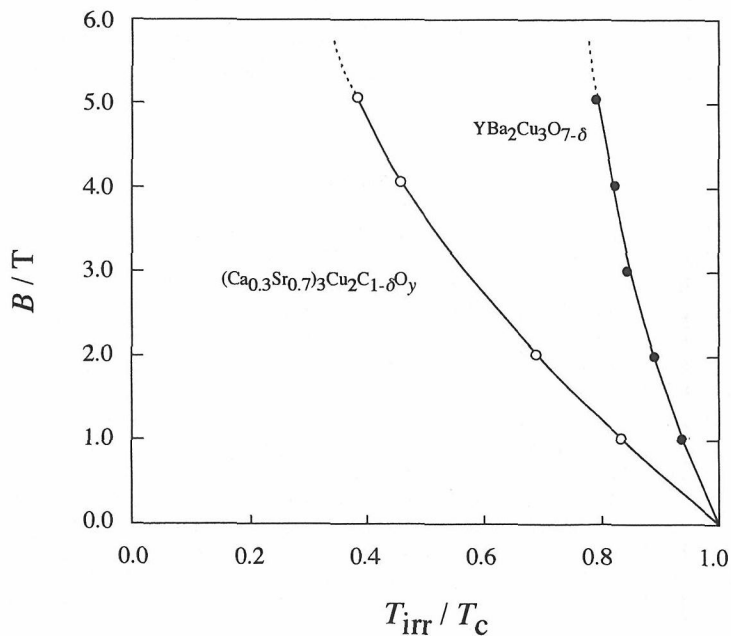


Fig. 7. Irreversibility lines of $(Ca_{0.3}Sr_{0.7})_3Cu_2C_{1-\delta}O_y$ (open circles) and $YBa_2Cu_3O_{7-\delta}$ (filled circles¹³).

ordering of carbon vacancies. The deficiency would give rise to hole carriers to be doped into the CuO_2 sheets. This may be consistent with the recent results on $(\text{Y}, \text{A})_3\text{Cu}_{2+x}\text{C}_{1-x-\delta}\text{O}_y$ by Miyazaki *et al.* suggesting that carbon vacancies produced after heat treatment under high oxygen pressure are the source of hole carriers.¹²⁾ Further experiments are, however, necessary to obtain a definite conclusion about the origin of the 4a-type superstructure of the present phase.

The irreversibility line of the present phase has been determined from split points between field cooled and zero field cooled curves at several magnetic fields up to 5T for the polycrystalline pellet, which is compared with that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ¹³⁾ as shown in Fig. 7. It is clear that the irreversibility field which measures the stiffness of the flux solid is lower in the present phase than in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, in spite of their similarity in T_c and crystal structure. It may be because the carbon atoms replacing the copper atoms at the chain sites of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ weaken the electronic coupling between a couple of CuO_2 layers, and thus the flux solid is easy to be destroyed owing to its two-dimensional character.

4. SUMMARY

A new cupric oxide carbonate superconductor $(\text{Ca}_{0.3}\text{Sr}_{0.7})_3\text{Cu}_2\text{C}_{1-\delta}\text{O}_y$ has been synthesized by using a high-pressure technique and its crystal structure and superconducting properties have been studied. The compound crystallizes basically in the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ type structure with a 4a-type superstructure, which has never been reported in other oxide carbonate superconductors. The irreversibility field is found to be much lower in this present phase than in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with nearly identical T_c and crystal structure.

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